Liquid–liquid phase separation and crystallization in binary polymer systems*

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The crystalline entities formed upon crystallization of semidilute (*ca.* 1 to 5%) solutions of polyethylene in poor solvents were examined, mainly by scanning electron microscopy. Due to a liquid–liquid phase separation process, these entities are small (*ca.* 1 to 10 μm), more or less spherical globules. Homogeneous and heterogeneous nucleation result in smooth and rough globules, respectively. Different thermal cycles were also investigated. The polymer globules offer a potential means of investigating the mechanism and kinetics of liquid–liquid phase separation. This phenomenom is also offered as an explanation for several unusual crystalline morphologies of polymers reported in the literature.

(Keywords: crystallization; phase separation; binary polymer systems; polyethylene)

INTRODUCTION

This paper is concerned with the genesis, morphology and structure of unusual crystalline entities formed in given polymer solutions when crystallization takes place after the solution has gone through liquid–liquid phase separation. For polyethylene solutions, the resulting morphologies are often (and mainly) small (*ca.* 1μm), roughly spherical particles, which have been described by Garber and Geil[1] as 'globules'. These authors, as well as Hay and Keller[2], have associated their formation with phase separation in the polymer solution but have not pursued their investigations further. Neither the unusual morphologies, nor the liquid–liquid phase separation in polymer solutions, which have been known for many years[3,4], nor even the link between them are therefore new. Yet, the phenomenon appears to have been largely forgotten or overlooked in the past and, despite renewed interest[5,6], in more recent work. A survey of the literature on polymer crystallization indeed reveals a number of 'abnormal' morphologies which may be explained in a rather straightforward manner when taking into account the possibility of liquid–liquid phase separation and resulting crystal growth in a confined space. An overview on this topic will be given at the end of this article.

We chose to study the liquid–liquid phase separation of polymer solutions and resulting morphologies by using polyethylene, since (i) its crystalline structure and morphologies are among the most thoroughly investigated[7], and (ii) a number of its solvents give rise to liquid–liquid phase separation, and the corresponding phase diagrams are known[8]. Furthermore, in this article we show that the analysis of the resulting morphologies may be a useful tool in understanding not only crystal nucleation and growth, but also the phenomenom of liquid–liquid phase separation itself.

EXPERIMENTAL

Materials

The polymer most often used in this investigation is a high density polyethylene of industrial origin (Du Pont) with $M_w = 12\,000$ and $M_w/M_n = 4.5$. The influence of the molecular characteristics of the polymer were not investigated in this study.

The solvents used included amyl acetate (distilled prior to use), benzaldehyde, biphenyl and isoamyl acetate, diphenyl ether and benzophenone (used as received).

Methods

Solutions of known concentrations were obtained by dissolving the polymer at 160°C to 180°C, in the solvents containing a few ppm of an antioxidant (Ionol). The solutions were introduced by capillarity into thin walled glass tubes (typically, disposable pipettes) which were sealed. Thermal treatments were done in a Mettler FP21 microscope heating stage (temperature stabillity was equal to ±0.2°C) equipped with a temperature controller. The treatments were usually ended by quenching in ice–water.

Observation of the phase separation was followed by optical microscopy in transmitted light. Resulting crystalline morphologies were observed in phase contrast and crossed Nicols optical microscopy, by transmission electron microscopy (Hitachi HU 11CS) and scanning electron microscopy (JEOL 35 CS and Philips 501). For the latter techniques, sample preparation often involved selective dissolution of the solvents which are crystalline at room temperature (diphenyl and diphenyl ether) in chloroform. In some cases, however, the solvents were removed by sublimation under vacuum. Sublimation of the solvent results in the preservation not only of the crystalline structures obtained, but also of their actual

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location in the crystallization vessel. While this possibility has not been used to its full advantage in the present investigation, it may become of interest when working out the finer details of liquid–liquid phase separation.

BACKGROUND

Liquid–liquid phase separation and nucleation in dispersed systems

The crystalline morphologies described are associated with the occurrence of two different physical processes, namely a liquid–liquid phase separation which creates a large number of domains, followed by homogeneous or heterogeneous nucleation and crystallization in these domains.

These processes are now briefly presented, based mainly on the classical works of Richards[3] and Cormia *et al.*[9] and are accompanied by an experiment specifically designed to illustrate them visually.

(*1*) *The liquid–liquid phase separation.* A typical phase diagram of a polymer in a poor solvent is shown in *Figure 1*, as adapted from the classical book of Flory[4] and the paper by Richards[5]. The crystalline phase separates from a single phase only for temperatures and compositions indicated by the lines MN and QR. For a composition range between N and Q, the solution crosses, on cooling, three regions:

(i) at high temperatures, a domain (I) where the solution is isotropic;

(ii) at intermediate temperatures, a domain (II), delineated by the area NCQ within which a single phase is unstable: the polymer solution separates into polymer-rich and polymer-poor phases which are thermodynamically more stable (C is the critical point, T_c is the upper critical solution temperature, *UCST*). For low polymer concentrations, the polymer-rich phase separates into the form of small droplets in the polymer-poor phase when the thermal treatment is sufficiently fast.

(iii) at low temperatures, a domain (III) where the crystalline phase separates out of the solution. The phase boundary NQ represents the equilibrium melting temperature of crystalline phases obtained in this composition range. Crystallization takes place in two lower temperature regions (T_{het} or T_{hom}), depending on the presence or the absence of heterogeneous nuclei within the individual droplets.

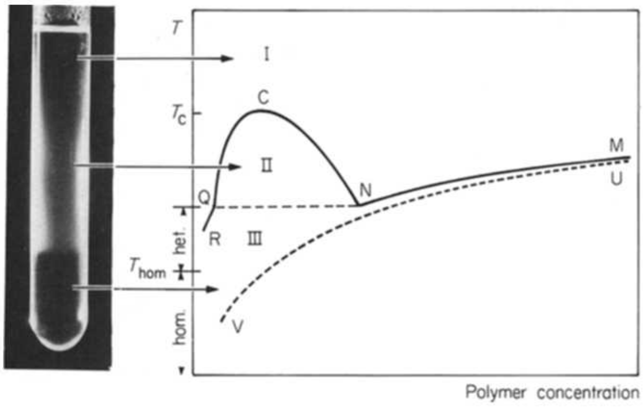

Figure 1 Schematic phase diagram of a monodisperse polymer in a poor solvent (solid line) and in a good solvent (broken line), as adapted from refs. 3 and 4. The existence of three important domains for a polymer-poor solvent system is highlighted in the photograph on the left of a polyethylene–benzaldehyde solution submitted to a sharp temperature gradient (see text)

Liquid–liquid phase separation and crystallization in the droplets can be vividly illustrated by a simple test-tube experiment. For this purpose, we developed and adapted an observation made by Cormia *et al.*[9]. The experiment is based on the use of a moderately concentrated solution of PE (here of $M_w = 20\,000$) in a poor solvent, the refractive index of which matches that of crystalline PE ($n \simeq 1.54$). For the experiment shown in *Figure 1*, benzaldehyde with $n = ca.$ 1.546 was selected.

The test-tube was heated to a temperature close to the boiling point of benzaldehyde, where the PE dissolved. The bottom of the tupe was then dipped in cold water, thus establishing a sharp temperature gradient. The test-tube then displays a section in the phase diagram of benzaldehyde and PE at fixed concentration as a function of temperature. The observed three zones indicate:

(i) at high temperatures (top of the tube), the existence of a clear isotropic PE solution;

(ii) at intermediate temperatures, the development of the liquid–liquid phase separation. The observed turbidity indicates that the droplets of concentrated polymer solution have a refractive index different from that of the liquid 'matrix' of dilute solution;

(iii) at lower temperatures, the crystallization of PE in the droplets, which brings the refractive index close to that of the solution (*ca.* 1.54 for both), and shows up as a 'clearing' of the solution.

Phase diagrams as shown in *Figure 1* were first established by Richards[3] for a low density polyethylene (the only type of PE available at that time) of M_w *ca.* 5000 in amyl acetate and in nitrobenzene. Nakajima *et al.*[8] determined similar phase diagrams for linear polyethylene in a number of solvents, including aliphatic alcohols, phenols, esters, ketones, biphenyl and biphenyl derivatives. A whole range of solvents was therefore available for the present investigation. While benzaldehyde is useful for illustrating the phenomena optically, other solvents indicated in the experimental section were preferred for any one of the following reasons: greater thermal stability, better solubility of PE and therefore acceptably high *UCST*, high boiling temperature, crystallization of the solvent above room temperature (which results in easy handling of the crystallized solutions, for example for biphenyl*), easy evaporation and/or sublimation.

(*2*) *Crystallization of small droplets: heterogeneous and homogeneous nucleation.* Crystallization of small PE droplets produced by a process that is essentially a liquid–liquid phase separation has been investigated in some detail by Cormia *et al.*[9] and later by Ross and Frolen[10]. The phase separation produces a number of droplets (*ca.* 10^{13} per gram) much larger than the number of heterogeneous nuclei present in the solution from the beginning (*ca.* 10^{10} per gram), and therefore makes it possible to investigate both heterogeneous and

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* Several polyethylene–organic solvent systems have been investigated, which give rise to eutectics (e.g. Smith, P. and Pennings, A. J. *J. Mater. Sci.* 1976, **11**, 1450; Smith, P. *Thesis*, University of Groningen, 1976). However, for the present PE–biphenyl system, the melting temperature of the diluent is well below 110°C, calculated by these authors as a lower T_m limit of the diluent for the formation of a eutectic. At any rate, if a eutectic solid is formed, its composition would be very close to a pure solvent.

homogeneous nucleation in polymers. Heterogeneous nucleation takes place at $T_{het} = 120°C$, and homogeneous nucleation takes place in a *ca.* 2°C temperature interval (near to 94°C and 79°C, for Igepal and dibutyl phthalate as suspension media respectively). The temperature ranges vary not only with the suspension medium of the droplets, but also with the cooling rate, and in particular with the molecular weight of the polymer.

The above results indicate that for investigation of the liquid–liquid phase separation and crystallization, domain (III) in the phase diagram of *Figure 1* should be divided in two sub-domains, depending on whether the quenching temperature is below or above T_{hom}.

RESULTS AND DISCUSSION

(*1*) *Phase diagrams*

Experimental phase diagrams have been established for the PE of $M_w = 12\,000$ used in this study, and for biphenyl and diphenyl ether as solvents. The curves corresponding to the low polymer concentrations used in the present investigation are shown in *Figure 2*. These curves were established by plotting the temperature at which phase separation is observed microscopically. The thermal treatments used involve a 1°C per minute stepwise decrease of the solution temperature. Phase separation is indicated by the formation, preferably on or near the capillary walls, of small spherical domains of *ca.* 1 μm diameter. The experimentally determined curve is by no means an equilibrium curve, since kinetic factors are involved. Both curves show the typical decrease in temperature at high concentrations, which is characteristic of the liquid–liquid phase separation. It was not possible to determine the *UCST* of the curve for the dilute diphenyl ether solutions. Also, birefringent entities were observed to grow for biphenyl solutions maintained at *ca.* 105°C, for all concentrations investigated. These entities will be further analysed in the following sections.

(*2*) *Thermal histories and associated crystalline morphologies*

The simplest thermal histories that can be envisaged involve heating above the *UCST* of the solution followed by:

—Direct quench to the crystallization temperature T_{cryst}. As indicated above, the resulting morphologies depend on whether T_{cryst} is located above or below the T_{hom} region. A special situation has also been observed in which crystallization of the solvent interferes with the crystallization of the polymer.

—A 'ripening' of the liquid–liquid phase separation by keeping the solution in the bell-shaped region of the phase diagram, followed by quench to low temperatures. As will be seen, this procedure makes is possible to investigate the kinetics and mechanism of the phase separation.

Direct quench to temperatures below T_{hom}. This fast quench procedure to $T_{cryst} < T_{hom}$ was typically achieved by dipping the capillary into ice water.

The polymer precipitate, obtained when a solution of polyethylene in amyl acetate or benzophenone is quenched to 0°C, is shown in *Figure 3*. It consists or more or less spherical objects with diameters in the μm range which we will name, following Garber and Geil[1] 'globules'. Scanning electron microscopy actually reveals the existence of two different types of globules (*Figure 4* and *Figure 5*): (i) a vast majority of small (*ca.* 1 μm diameter), smooth (within the resolution of the scanning electron microscope) particles. When properly oriented, these particles have small, straight depressions giving them an overall aspect of a plum; (ii) a small number of particles which, in sharp contrast to the previous ones, have a rough surface. The size of these particles is much less uniform and ranges from about 1 to 10 μm. The proportion of these particles is estimated to be on the order of one per thousand.

With reference to the above discussion on phase separation and homogeneous and heterogeneous nucleation, a simple scheme for the existence of two types of globules suggests itself. During the quench, the polymer solution phase-separates, giving rise to a large number of concentrated domains. Some of these domains surround ('encapsulate') heterogeneities in the solution, such as foreign particles, which act as nuclei in the liquid–liquid phase separation. Such an encapsulation is a well known phenomenon, much used in pharmacology[11]. On

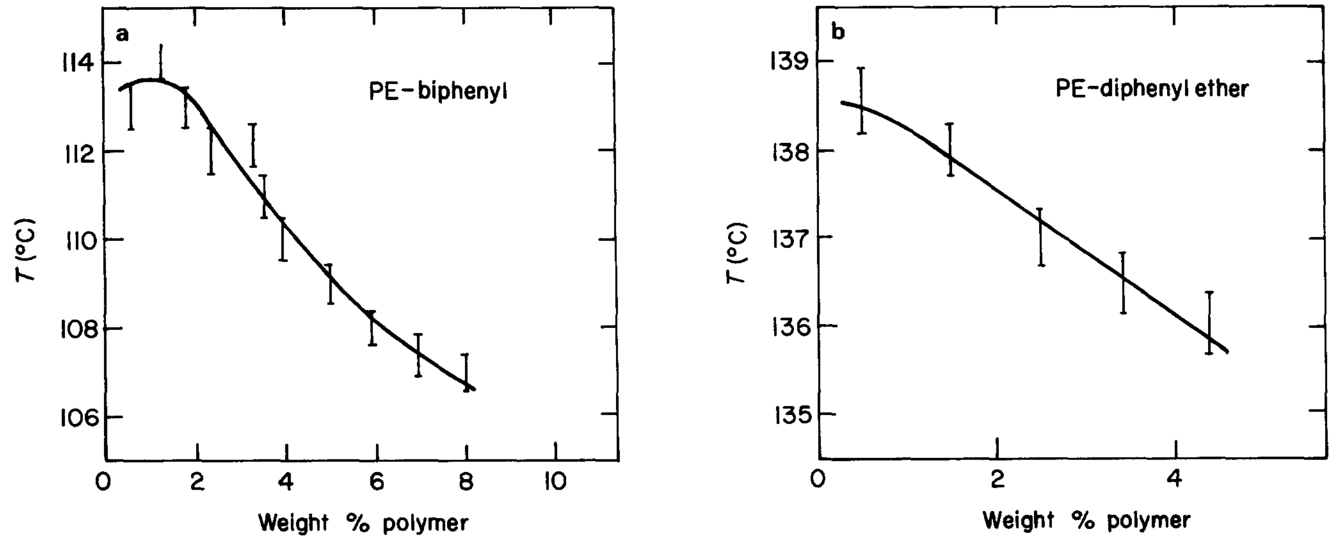

Figure 2 Experimental phase diagrams of binary (a) PE–biphenyl and (b) PE–diphenyl ether systems. Vertical bars correspond to the estimated error in the optically determined cloud points

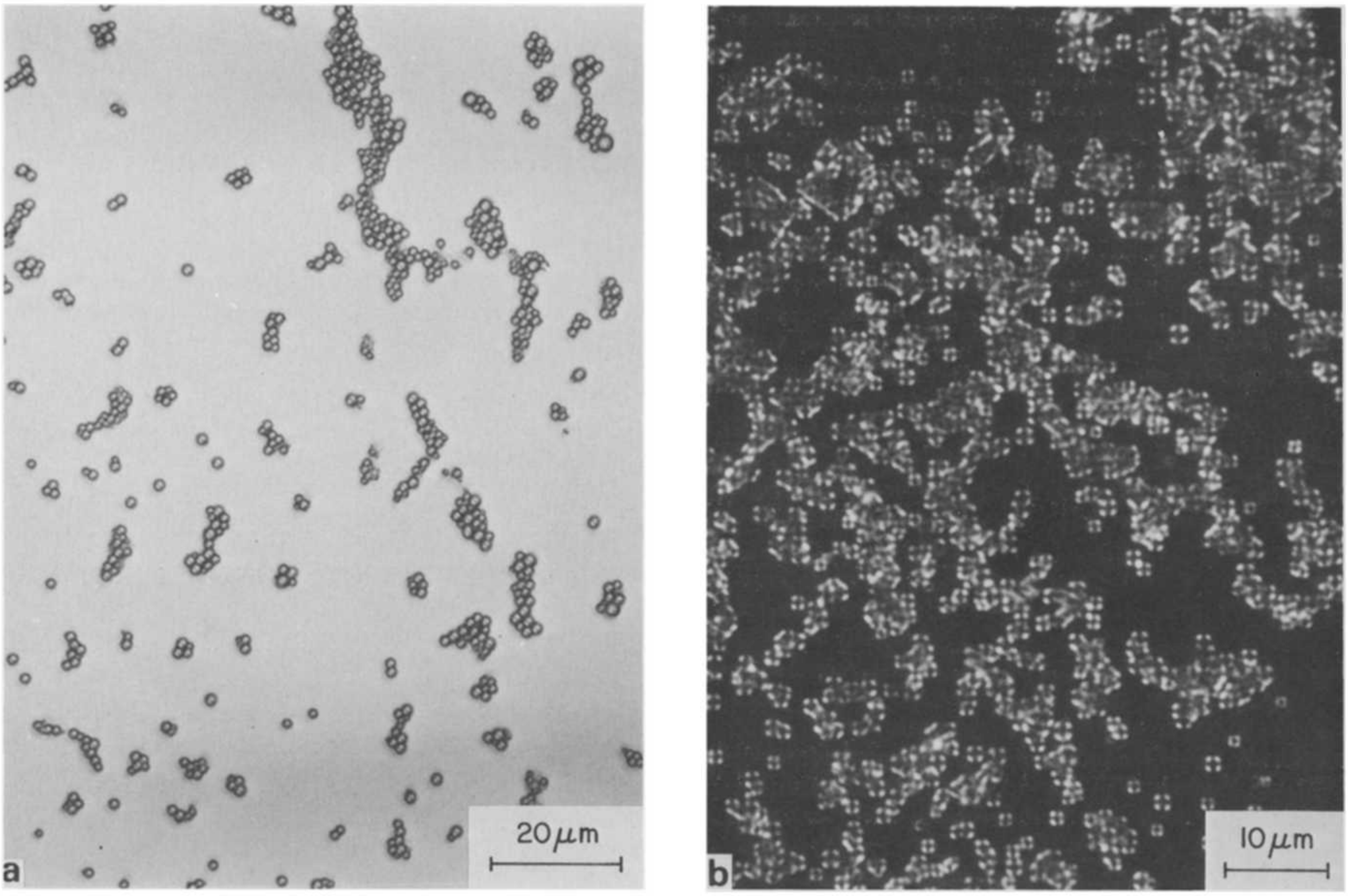

Figure 3 Precipitated particles from quenched solutions as seen (a) in phase contrast optical microscopy (left hand side: PE–isoamyl acetate system) and (b) under cross polars (right hand side: PE–benzophenone mixture)

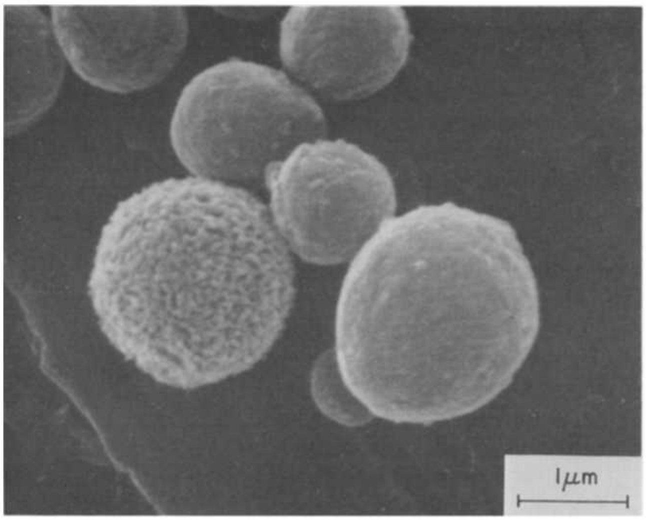

Figure 4 'Rough' and 'smooth' (within the resolution of the instrument) globules of PE obtained by quenching to 0°C a PE solution in isoamyl acetate (scanning electron micrograph)

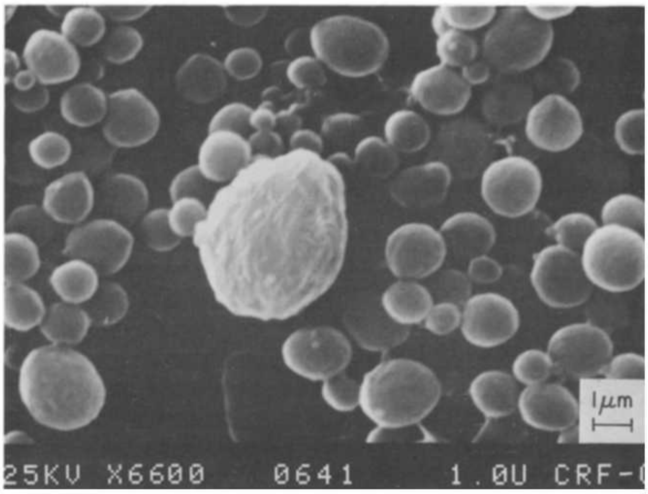

Figure 5 'Rough' and 'smooth' globules formed on quenching to 0°C a solution of PE in benzophenone (scanning electron micrograph)

further cooling, the heterogeneities may also act as seeds for polymer crystallization and initiate lamellar growth on their surface. Lamellar growth is thus directed outwards, as is the case in spherulitic growth. Lamellae or stacks of lamellae therefore stick out of the surface of the droplet which results in the observed roughness of the larger globules. The variable sizes of the rough globules reflects mainly the size distribution of foreign particles present in the solution if no significant droplet growth takes place on quenching.

The smaller, smooth particles appear to result from the crystallization of heterogeneity-free droplets of concentrated polymer solution produced in the phase separation process. As already mentioned, the number of droplets in this rapid quench is much larger than the number of heterogeneities present in the polymer solution. The interesting and unexpected feature of this crystallization is that it gives rise to *smooth* globules, which is not compatible with a radial growth of polymer lamellae as observed in the rough particles. In contrast with the rough particles, it appears that the exterior of the smooth particles is the fold surface of crystalline lamellae. In these germ-free droplets, nucleation (in the present case homogeneous nucleation) seems to take place at or very near the interface with the dilute phase, and growth follows this same interface. The resulting entity is therefore a nearly closed, bowl-like, lamellar structure in which the chain direction is *radial* relative to the centre of the globule. Furthermore, the smooth globules are likely to be hollow, or partly so, since crystal growth of the globule can take place only if it is 'fed' by polymer present in the concentrated solution inside. The above scheme also explains the linear depression observed in the smooth globules. As it is depleted, the concentrated solution tends to form a smaller droplet, thus resulting in increased curvature of the outer surface. The growing edges of lamellae will therefore be forced to bend further inwards when crystallization is almost complete, i.e. at the time when they are about to meet, on the opposite side of the droplet to where crystallization had started.

While the above scheme is a direct outcome of our observation of smooth globule surfaces, it suggests that the surface of the droplets is a preferred nucleation and crystal growth site. This in turn implies a local difference in polymer conformation or concentration near the phase boundary, although our experiments cannot discriminate between these two factors.

Quench to $T_{cryst} > T_{hom}$. This procedure involves the formation of liquid–liquid phase separation and heterogeneous nucleation only. These conditions are met when the polyethylene solution in biphenyl is quenched to *ca.* 100°C.

The resulting crystalline morphologies are shown in *Figure 6a* and *6b*. They are large assemblies of nearly flat lamellae much reminiscent of the so-called 'axialites' described by Bassett and Keller[12]. In such multilamellar objects, the growth of the individual lamellae is topologically restricted by their neighbours[13].

The crystalline entities of *Figure 6* appear to be an ultimate growth stage of the rough globules seen in *Figures 4* and *5*. They originate from active foreign heterogeneities embedded in phase separated droplets of concentrated polyethylene solution. During crystallization, after exhaustion of the polymer in the droplet (a stage shown in *Figures 4* and *5*), growth continues in the dilute polymer phase. The dilute phase concentration is kept constant by polymer transferred from polymer-rich droplets devoid of active heterogeneities, i.e., the germ-free liquid droplets act as reservoirs of polymer for the crystallizing droplets. As a result, the crystalline morphology does not reflect the liquid–liquid phase separation that takes place in the solution. On the other hand, in the direct quench to $T_{cryst} < T_{hom}$ examined previously the crystalline morphology better reflects the liquid–liquid phase separation since transfer of polymer has no time to take place: the potential supply of polymer present in the germ free droplets is 'frozen-in' by homogeneously nucleated crystallization.

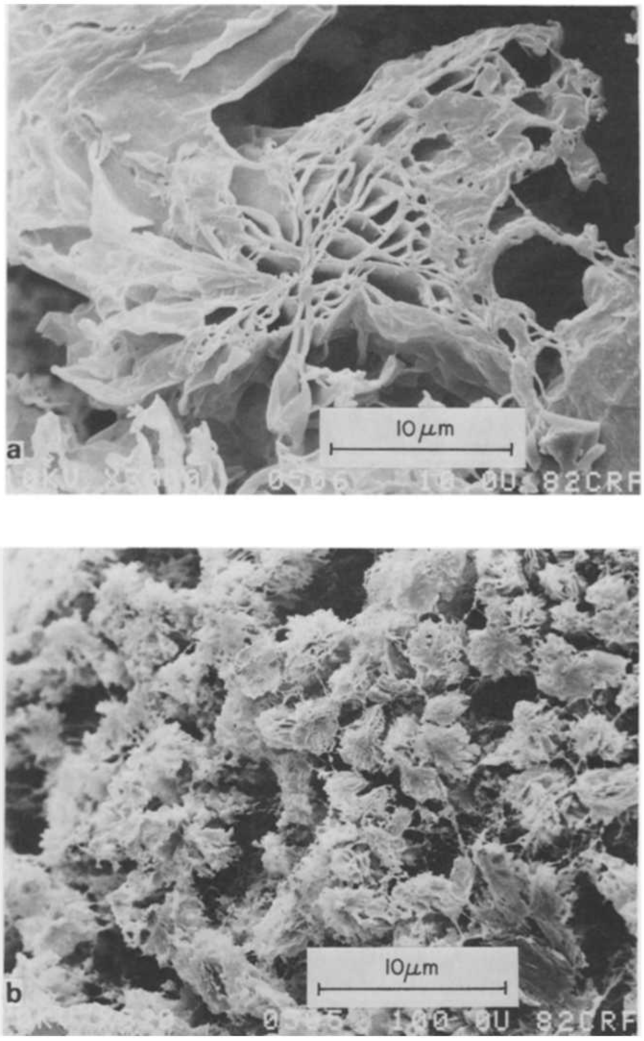

Figure 6 Two scanning electron micrographs (a) and (b) of multilamellar assemblies obtained by crystallization of a PE/biphenyl solution at 100°C for 10 min. After completion of the crystallization, the solution has been quenched to room temperature, and the solid biphenyl removed by sublimation under vacuum

Direct quench with interference of the solvent crystallization. Direct quench of biphenyl PE solutions in ice–water (i.e., at $T < T_{hom}$) gives rise to a somewhat different crystal morphology which, however, lends further support to the proposed crystallization scheme. *Figure 7* shows small globules of *ca.* 1 μm maximum size, indicating again phase separation of the type observed in isoamyl acetate or benzophenone (*Figures 4* and *5*). In contrast with the latter samples however, the surface of all these globules is rough and quite clearly displays lamellae or stacks of lamellae seen edge-on. Also typically, the lamellae seem to originate from one end of the globules rather than from their centres: lamellar stacks are more or less parallel to the longer dimension of the globules.

The different morphology of the globules indicates that the homogeneous nucleation scheme described previously is not operative in the PE–biphenyl phase separated system; on cooling another nucleation mechanism becomes operative at a temperature higher than the homogeneous nucleation. This different process appears to be nucleation by the crystalline solvent.

The crystallization temperature of biphenyl is *ca.* 70°C. This temperature is not far removed from the critical temperature range where homogeneous nucleation takes place in bulk polyethylene. In view of the solubility of PE

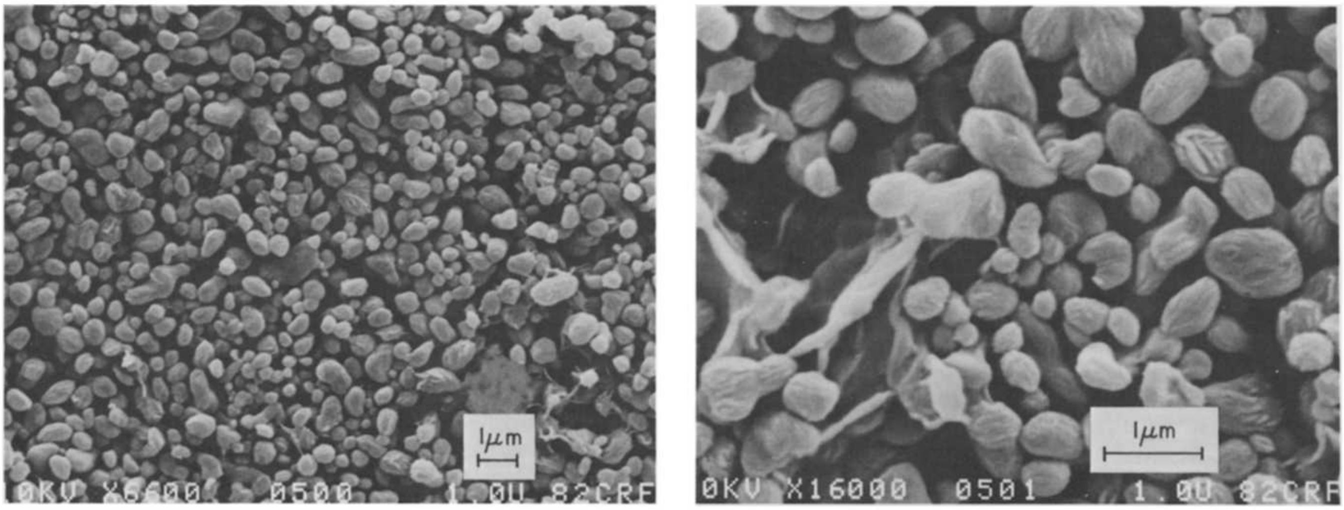

Figure 7 General (left) and close-up (right) SEM views of PE globules crystallized upon contact with solidified biphenyl. Note the irregular shape and roughness of all the globules

in biphenyl and the low M_w of the sample used in this study, homogeneous nucleation may well take place at temperatures lower than 70°C. Germ-free droplets, therefore, remain liquid down to the crystallization temperature of biphenyl. As the crystallization front of the solvent reaches the droplet, it induces the directional crystallization of PE.

The ability of biphenyl crystals to initiate the crystallization of PE is not surprising, but is brought to light only by the very specific experimental conditions created in the present investigation, where PE remains in solution down to 70°C. In a previous investigation[14], it was shown that the crystals of linear polyphenyls (typically *p*-terphenyl) are suitable substrates for the epitaxial crystallization of PE. Specifically, PE crystallizes on the (001) plane of *p*-terphenyl which provides a satisfactory lattice match with the (100) PE planes. Furthermore, the (001) planes of linear polyphenyls are isomorphous, which implies that biphenyl crystals can induce the same epitaxial crystallization of PE as *p*-terphenyl.

Two step thermal cycle with isothermal nucleation and growth of liquid domains. For this particular two-step thermal cycle, the solution was maintained at temperatures between T_C and T_N (or T_Q cf. *Figure 1*) for some time, i.e., in the miscibility gap (region II) of the phase diagram. This was typically at 106°C for the present PE sample dissolved in biphenyl.

On quenching these solutions in ice–water, two types of globules are observed: small globules that result from the quenching (cf. *Figure 7*), and larger ones which result from the crystallization of large globules produced at 106°C. Under the experimental conditions used, the phase separation indeed takes place through a classical nucleation and growth process, and yields fairly large droplets of rather uniform size.

Quenching a phase-separated polymer solution therefore appears to be a means of investigating the phase separation process itself, since the crystalline PE morphology reflects that of the concentrated polymer phase. This correspondance may not be absolute however. In this respect, we note that a fair fraction of globules obtained in the present thermal cycle appeared to be hollow, or more precisely, invaginated (*Figure 8*). The invagination must result from the crystallization process and, more specifically, from the depletion of PE on crystallization. As already indicated, if the crystal growth follows the globule walls, consumption of PE results in a shrinkage of the droplet, i.e., reduction of its diameter, and increasing curvature of the lamellar crystals. Provided such corrections are taken into account, the present polymer globules give an acceptable, 'frozen-in' picture of the liquid–liquid phase separation and offer a clear potential for further investigation of this widespread physical phenomenom.

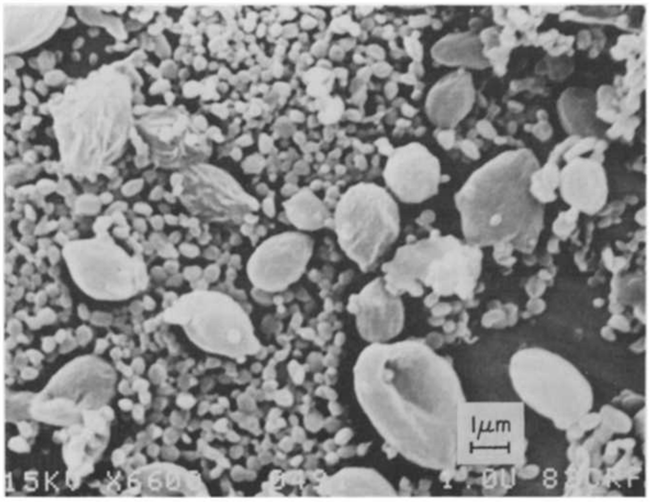

Figure 8 Globules of PE obtained after quenching to room temperature a solution of PE in biphenyl initially maintained at 106°C for two minutes. Note the background of small globules which are similar to those of *Figure 7* and which were formed on quenching. The larger globules are representative of the stage of growth reached at 106°C, just before the quench, by the liquid polymer-rich globules. Some of them become invaginated upon crystallization (see text) (scanning electron micrograph)

(3) *Liquid–liquid phase separation and crystalline morphologies of other crystallizable polymers*

In the present work, the crystalline morphologies associated with and resulting from liquid–liquid phase separation were investigated for polyethylene only. This phenomenon, though, is widespread and occurs in many polymer solutions. It importance in the formation of physical gels obtained with more concentrated systems has been recognized[15]. It appears, however, to have been overlooked as a possible explanation for a number of unusual morphologies reported in the literature for more dilute polymer solutions. In the following discussion, we will refer specifically to (i) the widespread observation of globules of a number of crystallizable polymers; (ii) the formation of 'hollow fish-bowl like crystals' reported by Khoury and Barnes for polyoxymethylene (POM)[16], poly(4-methyl pentene-1) (P4MP1)[17] and poly(chlorotrifluoroethylene) (PCTFE)[18]; (iii) the formation of semi-hexagons or strings of semi-hexagonal crystals of poly(benzyl L-glutamate) (PBLG) reported by Price *et al.*[19].

Formation of polymer globules. The formation of polymer globules has already been linked with liquid–liquid phase separation. Crystalline globules have been reported for a number of polymers[1,2,20]. They are consistently obtained when using rather poor solvents, while for good solvents a drastic quench procedure is necessary, but may not be sufficient. For example, we have often observed the formation of polymer globules in association with epitaxial crystallization for benzoic acid solutions of polyethylene[14] or polyamides[22]. The shape of the resulting globules depends on the particulars of the crystal growth. For example, polyamide globules tend to be elongated and have an empty cigar-like shape due to preferred growth along the hydrogen bond direction. It remains that with the right combination of solvent, concentration and thermal history, globules can probably be obtained more easily than single crystals from most crystallizable polymers, especially from those that are the least soluble.

Hollow 'fish-bowl' like crystals. Khoury and Barnes made a detailed investigation of single crystals of P4MP1[17], POM[16] and PCTFE[18] grown over a wide temperature range: typically, T_{cryst} of 130°C to 80°C for P4MP1 in amyl acetate. They observe that the single crystals, which are nearly flat at 130°C, tend to curve at lower T_{cryst}, and are 'all the more pronouncedly curved the lower the crystallization temperature'[16]. Khoury and Barnes propose a crystallographic interpretation of this curvature of the lamellae: they suggest that it is 'a cumulative consequence of the intrinsic conicalness of the sectored outgrowths which develop in successive arrays at their periphery and is governed by the frequency (per unit path length from pole to periphery) at which new sectored outgrowths are generated during the growth of the lamellae, the higher that frequency the smaller the radius of curvature of the lamellae'[16].

Based on the present results, we suggest that the formation of bowl-like crystals as described by Khoury and Barnes is yet another manifestation of liquid–liquid phase separation. The argument rests for the one part on the inability of the proposed mechanism to account for the progressive change of orientation of the *chains* in the crystal. In tent-like ('conical') crystals, chains of the two crystal sides are parallel; repetition of a tent-like morphology cannot result in the dramatic changes of chain orientation observed in the bowl-like crystals (more than 180° between the chains crystallizing first and last). For the other part, the argument also rests on the observation of features that occur upon crystallization of a liquid–liquid phase separated system. For example, Figure 29 of ref. 16 shows large bowl-like crystals with several smaller ones grafted onto them. This morphology is expected when small germ-free globules happen to touch an already solidified globule. Similar examples have been observed in the present work and are visible, for example in *Figure 8*. If this interpretation is correct, the formation of nearly perfect bowls must be associated with the high symmetry of the crystal lattices of P4MP1 (tetragonal) or POM (hexagonal). We have also observed nearly perfect bowl-like crystals for a sample of poly (D,L-benzyl glutamate) (hexagonal unit cell) crystallizing in dioxane. Also as a consequence, the formation of more curved crystals (i.e., crystals of smaller size) at low temperature is compatible with a liquid–liquid separation process which creates more domains at low temperature. On the contrary, the very continuous transition from flat crystals at high T_{cryst} to distinctly curved crystals at low T_{cryst} seems in contradiction to the existence of a clear transition that would be expected from the phase diagram. Other variables, not yet analysed, may intervene in the process. Clearly, in view of the progressive change in morphology and the very simple shapes (linked with their high symmetry), P4MP1 and POM appear to be polymer probes well suited for the investigation of the liquid–liquid phase separation referred to above.

Semi-hexagons of PBLG. Price *et al.*[21] have grown single crystals of PBLG from solutions in hexafluoroisopropanol (HFIP). Later, Price *et al.*[19] reported curious morphologies obtained upon crystallization in similar solutions, i.e., hexagonal single crystals that are halved, but not necessarily along a definite crystallographic axis and also rows, or strings, of such crystal halves. No explanation for these quite unusual crystal morphologies was offered.

We suggest that these morphologies result from crystal growth in a confined space created by a liquid–*liquid crystal* phase separation. HFIP is known to be a rather poor, weakly hydrogen-bond breaking solvent for PBLG. In the present case, PBLG phase separates into elongated lyotropic liquid crystal domains. Nucleation of the crystallization occurs at or near the domain walls and, contrary to the case of PE, propagation towards the outside is reduced or suppressed by the low polymer concentration of the surrounding medium. Following this scheme, the rows of semi-hexagons simply reflect the path and the topology of the phase separated, liquid-crystalline domains of PBLG. Phase separation in the polymer solution prior to crystallization appears again to be responsible for these unusual crystal morphologies.

CONCLUSIONS

Polymer crystals formed in poor solvents have atypical morphologies, quite different from those of single crystals formed in good solvents. These morphologies reflect the interplay of a liquid–liquid phase separation process and nucleation of the polymer crystals. In the simplest thermal history—direct quench to low T_{cryst}—the resulting morphologies are small globules. While these globules and their origin via liquid–liquid phase separation were known, the present work has shown that:

(1) Globules formed via heterogeneous and homogeneous nucleation can easily be distinguished by

scanning electron microscopy. Homogeneous nucleation takes place at or near the surface of the globules and growth proceeds along the globule walls giving rise to smooth particles. This behaviour suggests a different polymer chain conformation or concentration at or near the concentrated/diluted solution phase boundary. Heterogeneous nucleation leads to rough particles with radial lamellae or stacks of lamellae.

(2) Different crystalline morphologies can be obtained depending on the specific thermal history of the solution. In particular, polymer crystallization can be used to 'freeze-in' the shape of the liquid phase separated droplets. This feature provides a potential means to investigate in great detail the liquid–liquid phase separation and its kinetics by observing the size of the droplets obtained at different quench times. The use of a solvent that can be sublimed makes it possible to analyse their distribution in space.

(3) Liquid–liquid phase separation phenomena that take place prior to crystallization can induce crystalline polymer morphologies quite different from classical single crystals obtained in dilute solutions. These different morphologies are governed by the topological restrictions to crystal growth set by the phase separation.

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